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Methanol Dissociation The Effects of Partial Dissociation

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Technical Report

Methanol Dissociation: The Effects of Partial Dissociation

By

William B. Clemmens

December 1984

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16. ABSTRACT

This report documents the work done in-house with simulated partial dissociation of methanol with the NAPS-Z methanol engine. EPA found that efficiency improvements when using dissociated methanol came from two sources. 1) The initial improvement came from the ability to run at a given lean f/a ratio with less cyclic variation and presumably fewer occurances of lean misfire. 2) The second part of the efficiency improvement came from the change-of-state of the liquid fuel to a dissociated fuel.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Methanol Dissociation: The Effects of Partial Dissociation

I. Introduction

The Office of Mobile Sources within the Environmental Protection Agency has studied and evaluated alternative transportation fuels since its formation in 1970. EPA's responsibilities under the Clean Air Act also have necessitated a significant regulatory role dealing with transportation fuels. In particular, Section 211 of the Clean Air Act requires EPA to play a key role in the introduction of new fuels and fuel additives. Perhaps most visible was EPA's role in the introduction of unleaded gasoline to permit the use of catalytic converters on 1975 and later model year automobiles. More recently EPA has responded to a growing interest in the use of oxygenates (in particular methanol) for use in motor vehicles and for blending with gasoline.

As part of this response to the interest of methanol, a program was undertaken to grade several fuel utilization concepts. One of those concepts that has been evaluated is what we have termed "partial dissociation." The process of dissociation is the break-up of one chemical combination into simpler constitutents. In the case of methanol fuel, the combination of CH_3OH is broken down with heat and a catalyst into a gaseous mixture of approximately 66 mole percent H_2 and 34 mole percent CO. The theoretical advantages of utilizing dissociated methanol over liquid methanol for engine fuel are two-fold. One, the energy of the dissociated mixture is approximately 10,000 BTU/lb versus 8,644 BTU/lb for liquid methanol. Potentially with the higher BTU content of the dissociated fuel, each gallon of liquid methanol can be utilized much more efficiently,because the heat needed to dissociate the liquid methanol can be obtained from the waste heat of the engine exhaust gas. And two, the nature of hydrogen combustion should allow engine calibrations that provide leaner operation which can imply in some cases better efficiency and lower emissions. Combined the two factors (enhanced energy content and hydrogen combustion) have the potential to improve the thermal efficiency by about one-fourth over and above the base efficiency, if the fuel is completely dissociated (see Section II.A). A maximum of about 16 percent improvement over the base can be derived from the energy enhancement alone. The balance of the improvement relates to how well an individual engine utilizes the enleanment allowed by the hydrogen addition.

Typically, however, the volume requirements for the catalyst and the heat exchanger necessary to dissociate all of the methanol used by the engine are quite large leading to vehicle space limitation problems. Also, the carburetor control system for large quantities of H_2/CO gas can be complex. Because the theoretical possibilities looked promising, the question was posed, "Is it possible to achieve a sufficient portion of the theoretical potential of full dissociation with some lower amount of dissociation and correspondingly less complex dissociation hardware?" In other words, can more space-efficient part load performance be obtained by splitting the energy flow to the engine, the major fraction being liquid methanol and the smaller fraction being passed through a compact dissociation reactor (with possibly better dissociation efficiencies), and could this combination result in a better overall package than attempting to dissociate the entire fuel flow in a large reactor which typically exhibits relatively poor dissociation efficiencies at part load?

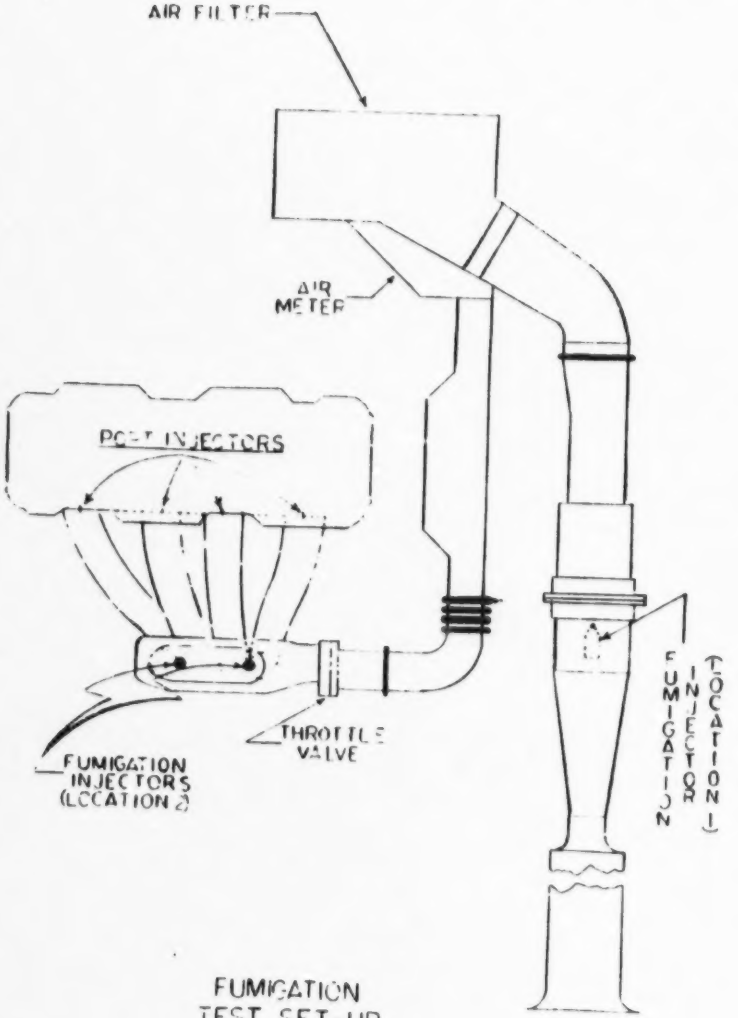
II. Summary

The results indicate that possibly as much as 40 percent of the potentially available improvements can be obtained utilizing only a 30 percent fraction of the simulated dissociation gas. However, the absolute magnitude of the improvement in efficiency at these fractional dissociation levels was somewhat limited. The method of energy accounting is critical to the level reported - up to 5 percent improvement by one technique and up to 10 percent improvement by the other. Also there appears to be a minimum level of dissociation necessary to obtain positive improvements in efficiency. This level coincided with improvements in emissions.

Highlights and observations of these results as well as conclusions drawn from them are presented in this section. Supporting analyses and technical information are contained in the following sections and appendices.

A. Procedure, Results, and Observations

To test the hypothesis, a series of tests were run on a Nissan 2 liter NAPS-Z engine converted to methanol operation. A mixture of hydrogen and carbon monoxide (H_2/CO) gas was injected into the intake manifold from cylinders of compressed gas to simulate low levels of dissociation (Figure 1). The amount of H_2/CO gas injected was approximately 4, 9, 18, and 30 percent by mass of the total energy flow to the engine. Note percent dissociation



FUMIGATION TEST SET-UP

FIG 1

Table II-1

Simulated Dissociation at 1500 RPM and 29.5 ft-lb

	Baseline	Simulated Dissociation Weight Fractions 4%	9%	18%	30%
% Dissociation					
BTU basis	-	5.5	11.6	26.4	53.4
Mass basis	-	4.5	9.1	18.5	31.4
Equivalence Ratio (for best results)	.69	.647	.701	.618	.583
Best Efficiency					
Thermal Efficiency (% BTE)	26.6	26.63	27.08	28.02	27.82
System Efficiency (% SYE)	26.6	26.58	27.44	28.88	29.29
Difference	0	0	.4	.9	1.5
% Improvement*					
BTE	-	0	1.8%	5.3%	4.6%
SYE	-	0	3.2%	8.6%	10.1%

*Compared to neat methanol baseline

is used in this paper to describe the mass fraction of the total energy consumed by the engine which was H_2/CO gas. (The total energy was assumed to be an equivalent amount of liquid methanol which implies a dissociation efficiency of 100 percent in a small reactor.)

Because of the complexity of the energy accounting, it was important to identify the two accounting techniques used to determine thermal efficiency. The distinction between the techniques is where the boundaries of the control volume are placed. Brake Thermal Efficiency (BTE) was calculated on an energy-out over energy-in basis (i.e. fuel entering the control volume boundary and power exiting). In our simulation the fuel crossing the boundary was a mix of methanol, H_2, and CO. However, if a dissociation reactor had been used, the only fuel crossing the control volume boundary would be methanol. The concept of System Thermal Efficiency (SYE) was developed to transform our measured BTE data into results that might be expected as an upper limit of performance (SYE) if a reactor had been used (an analytical description of this treatment is found in section VI-A).

With these conventions firmly in mind (BTE vs. SYE), the test results in Table II-1 indicate that modest improvements in brake thermal efficiency (BTE) were possible (on the order of 5 percent improvement). Figure 3* shows the trends of these results while Figure 2 indicates the baseline curve. However, system efficiency (SYE) improvements of up to 10 percent are calculated for the highest partial dissociation rate simulated, if the H_2/CO gas were assumed to come from liquid methanol, and if the conversion from liquid methanol through vapor phase to dissociation gas were complete (see Table II-1 and Figure 4).

To put these data in perspective, we compared our partial dissociation data to data on full dissociation (100% of total energy flow) reported by Hirota (Ref. 1).** Because Hirota used a true dissociation reactor, his results are in units of BTE. In order to compare our results to his, our SYE results

---

* Note: The Greek work "phi" is used to designate equivalence ratio throughout the report.

**Numbers in parentheses designate References at the end of paper. In Hirota's study(1), a dissociation reactor was used to provide the dissociation gas. Analysis of the gas indicated a mixture of components, the dominate species being H_2 and CO. For the purposes of comparison, it was assumed this mixture represented complete dissociation of the total engine fuel flow.

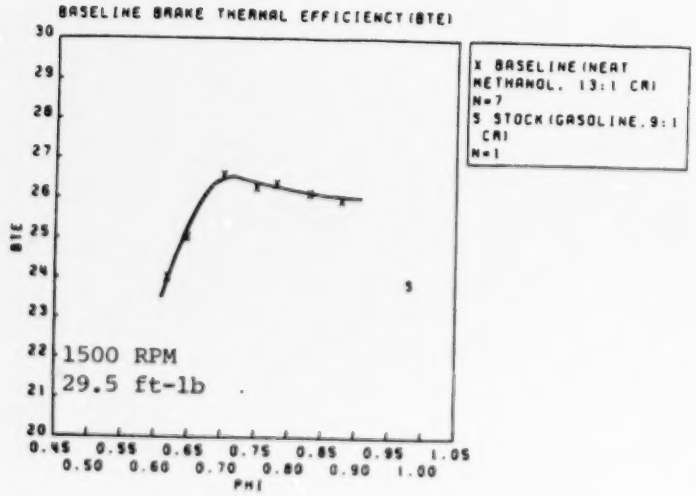


FIG 2

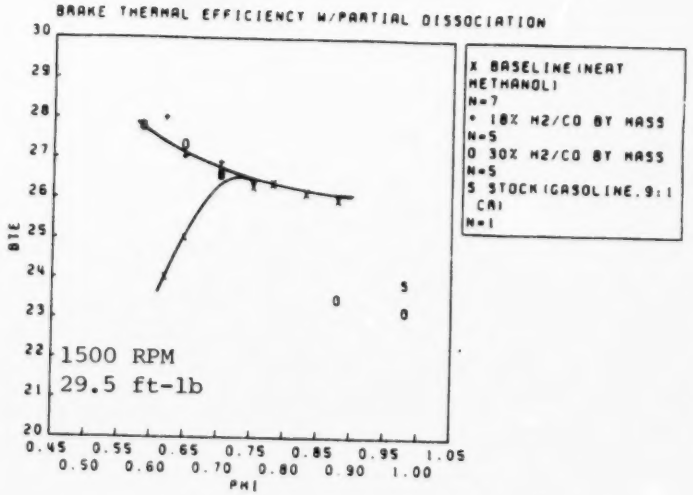


FIG 3

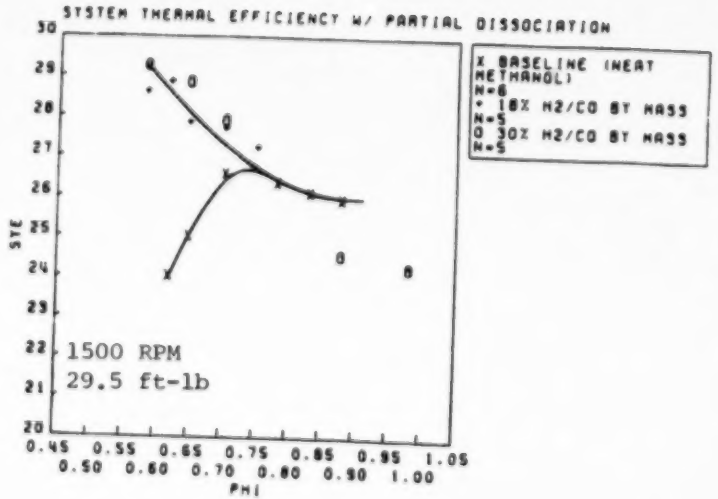


FIG 4

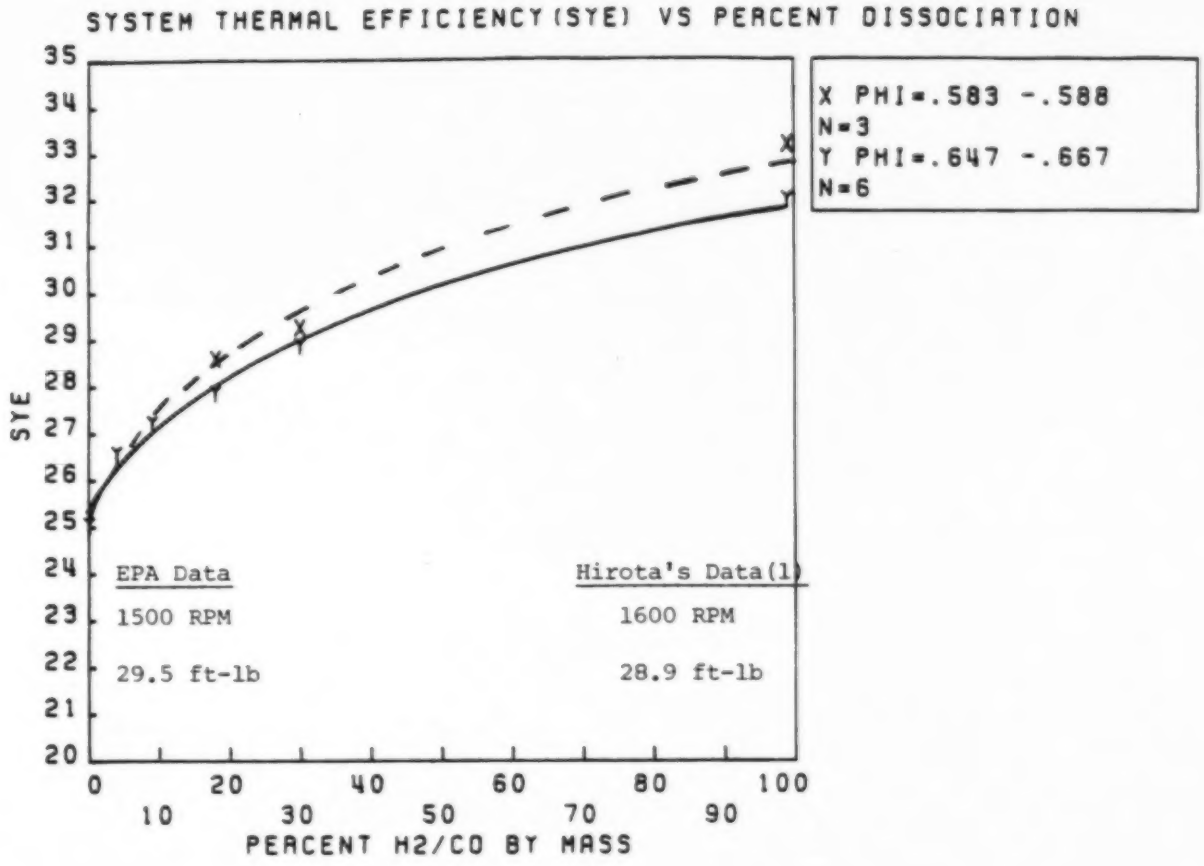

SYSTEM THERMAL EFFICIENCY(SYE) VS PERCENT DISSOCIATION
X PHI=.583 -.588
N=3
Y PHI=.647 -.667
N=6
SYE
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
EPA Data
1500 RPM
29.5 ft-lb
Hirota's Data(1)
1600 RPM
28.9 ft-lb
0
10
20
30
40
50
60
70
80
90
100
PERCENT H2/CO BY MASS

FIG 5

(which simulated the use of a reactor with optimum conversion efficiency) were compared to Hirota's BTE results. Figure 5 is a plot of this data (efficiency) versus the fraction of dissociation gas used. There is a great deal of interpolation between 30 percent dissociation (our highest limit) and 100 percent dissociation (Hirota's data) in Figure 5.* However, these limited results do suggest that there seems to be a greater fraction of improvement at the lower levels of dissociation than at the higher levels.

This observation is supported by several other factors involved in the dissociation process. First to digress a little, the source of the improvement in efficiency from the dissociation process appears to eminate from two separate processes. The initial process occurs by the introduction of hydrogen into the fuel. The amount of improvement seems to be tied to the ability of a particular engine to run leaner with less cycle to cycle variation when hydrogen is added than without the hydrogen addition. (The improvement in cyclic variation was readily apparent by subjectively observing the engine roughness during testing). To some extent this ability is governed by the lean limit. A review of the literature (see section VI-B) suggests that the improvement in the lean limit can be correlated with the level of hydrogen added to the fuel (HWF - hydrogen weight fraction), and suggests that the percentage improvement in the lean limit is greater at the lower to moderate levels of hydrogen addition. The second process involves the energy enhancement of the fuel resulting from the dissociation process. The maximum improvement from this source can be calculated from the lower heating value of the composite gases used which in our case was for a hydrogen and carbon monoxide mixture. Using the lower heating values (from Table III-1), we find that the value for our mixture of hydrogen and carbon monoxide is 16 percent higher than the value for liquid methanol. The improvement for the second process is therefore limited to 16 percent at 100 percent dissociation (see section VI-A). This maximum limit is, of course, proportioned based on the fraction of partial dissociation. The observed data suggest that this relationship also is not linear, and that a greater fraction of enhancement occurs at the lower rates of hydrogen addition to the fuel. (This may be due to the relationship between the hydrogen weight fraction (HWF) and the hydrogen energy fraction (HEF) - see Figure 12, section VI-B.)

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*In most cases, the data plotted in this report represent the average of multiple results. However, in some cases single data points were used. In general, the validity of those points is subject to how well they fit the trends of the other data.

Both sources of efficiency improvement from dissociating methanol, then, suggest that a greater fraction of improvement would be expected to occur at lower or partial dissociation rates, and supports the similar observation determined from the test data. From this we can conclude that while the hypothesis appears to be basically true (more change at low dissociation rates) , the potential improvements in system efficiency are not exceedingly large at the low rates - typically less than 10 percent improvements. If, however, we assume Hirota's (1) base engine on neat methanol* would have similar efficiency to our base engine (which is implied in Figure 5), full dissociation only nets around a 26 percent improvement over the base. From this aspect, our 10 percent improvement in SYE represents about 40 percent of the available improvement. An 8 percent SYE improvement would represent about 30 percent of the available increase. Since these improvements are approximately the results obtained for the 30 percent fraction and the 18 percent fraction respectively, we see that the return on efficiency at these lower rates may possibly exceed the fraction of dissociation necessary for that return. This perspective may justify the potentially less complicated hardware necessary for partial dissociation under certain conditions.

Another interesting aspect of the partial dissociation exercise is that the introduction of the hydrogen gas in the H_2/CO mixture might be considered an approximate method to simulate the effects of extending the lean misfire limit by some other means. If this assumption is accepted, then we might consider the brake thermal efficiency (BTE) (as opposed to system efficiency) with the H_2/CO gas as somewhat indicative of the BTE that could be achieved with liquid methanol if the lean limit were somehow extended by other means. Figure 3 indicates the baseline BTE performance with liquid neat methanol and the higher levels of H_2/CO addition as the equivalence ratio is changed. In the baseline case, leaning the engine down to about an equivalence ratio of about 0.69 (from about 0.85), improves the efficiency slightly; below 0.69 the BTE falls off dramatically (assumed to be the result of increasing misfires as evidenced by the increasing organic matter emissions in Figure (6). As evidenced from the 4 percent and 9 percent

*Hirota (1) did not provide data in his paper on any baseline operation on neat methanol. However, since he used a similar engine, a Nissan L20 versus a Nissan Z20, we felt such an assumption was justifiable to estimate the return from partial dissociation even though the estimate is sensitive to the baseline level.

data (reported elsewhere in this paper), doping the engine with small amounts of H_2/CO gas causes the improvement in BTE performance to continue somewhat below the 0.69 level, but then the BTE falls off as in the baseline case. Increasing the amount of H_2/CO gas to 18 percent and 30 percent appears to extend this fall-off point, and the BTE performance improvement was continued down to an equivalence ratio of 0.58. At this ratio, lean misfire was encountered even though the equivalence ratio was still considerably above the 0.45 lean flamability limit of methanol. However, prior to reaching the abrupt lean misfire limit, no fall-off in BTE performance was encountered, nor were any sudden increases in organic matter (OM) emissions evident (which appears to be indicative of BTE fall-off). It is also interesting to note that between an equivalence ratio of 0.70 to 0.75, the BTE performance of liquid methanol and partially dissociated methanol is for all practical purposes the same.

If the preceeding scenario is an appropriate representation of the hydrogen addition, then the partial dissociation gases could be construed as an "ignition enhancement device" for lean methanol operation. Some support for this perception is reported by Inagaki, et al. (13) suggesting that the minimum ignition energy for reformed or dissociated gas is on the order of 10 times less than that needed for gasoline. Inagaki did not report a comparison with neat methanol, but such a comparison would be expected to be of the same order of magnitude in that the required ignition energy between gasoline and methanol is generally accepted to be about the same (typically 0.25 MJ for gasoline and 0.23 MJ for methanol). Therefore, it seems logical that the fractional dissociation would enhance the initial rate and the completeness of combustion through an improved ignition reserve potential relative to neat methanol. Both factors (combustion rate and completeness) are generally believed to be advantageous to lean engine operation with good efficiency.

Complicating the effectiveness of the potential ignition enhancement of partial dissociation is that a minimum amount of dissociation seems to be required to obtain efficiency improvements with lean mixtures (details are in section VI-C). Otherwise efficiency losses (from optimum with 100% liquid methanol) occur. This minimum required dissociation (MRD) level appears to be around 12 or 13 percent dissociation as a fraction of the total fuel flow at the primary test point, (1500 RPM, 29.5 ft-lb). At a lower load point the MRD level seemed to increase to between the 20 percent and 34 percent dissociation levels (no test points were run between these values to narrow the increment).

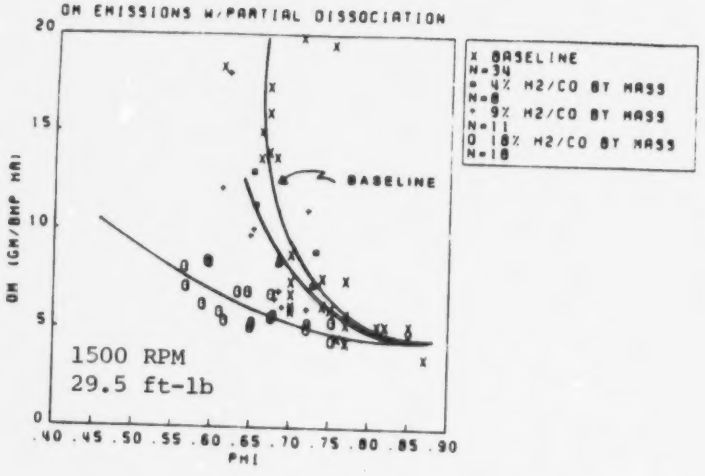

FIG 6

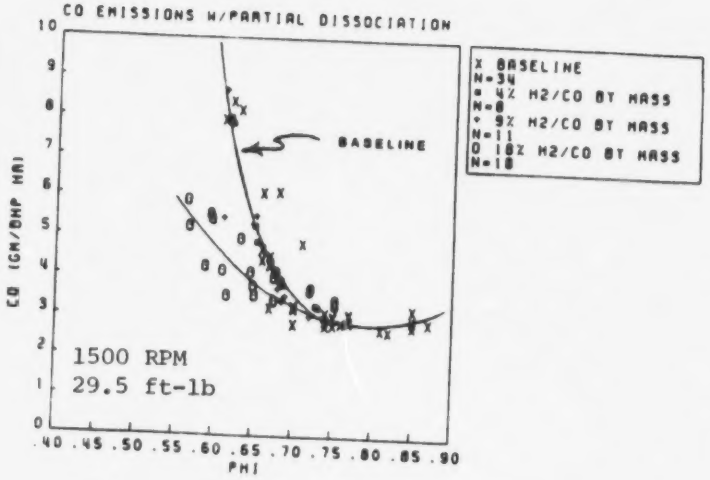

FIG 7

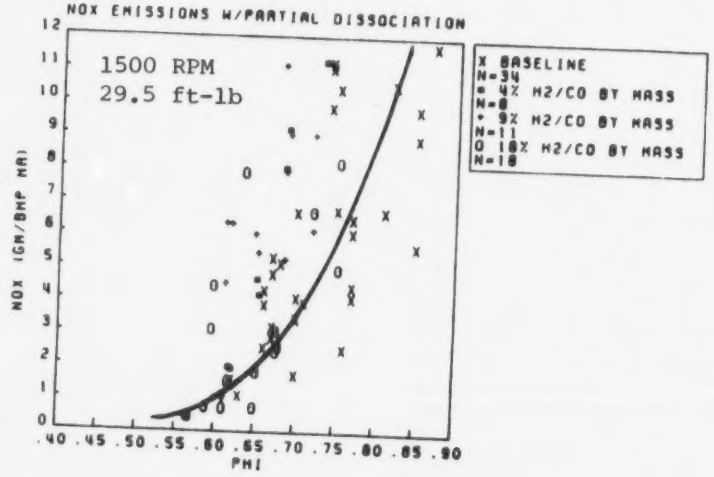

FIG 8

Engine emission results from a limited series of tests are presented in Figures 6, 7, and 8 plotted against the actual equivalence ratio. OM* and CO tend to follow the classic lean misfire trends. They seem to be affected by the level or fraction of dissociation gas used. The trend in HC and CO at the 18 percent level are what one might expect from improved burn rate, and this improved emission performance corresponds with the improved efficiency that appeared to occur above the MRD level. Therefore, the emission data would tend to support the hypothesis that a minimum level of dissociation is required for an efficiency improvement. NOx emissions seem to be primarily dependent only on overall equivalence ratio.

Since both the minimum dissociation (MRD) level and emission results tend to support an ignition enhancement role for small fractions of dissociation, it seems reasonable to pose the question, "are there other means of ignition enhancement that are as effective, less costly, less complex, and possibly more predictable?" Improvements to the standard ignition system are a first thought, and we have seen some slight improvement with this approach. Of course, plasma ignitors have generally been tried by various researchers on gasoline fueled SI engines with mixed results. One possibility that apparently hasn't been tried is to move the source of the dissociation gas closer to the spark plug. In other words, create a locally rich mixture of dissociation gas near the spark plug at the time of ignition, rather than fill the whole chamber with dissociation gas (i.e., the stratified approach could reduce the amount of dissociation gas needed). Three possibilities to achieve this stratified ignition mixture are (1) deliver the dissociation gas directly to the plug or the vicinity of the plug (possibly in a prechamber), (2) utilize some dissociation catalyst material within the spark plug (a plasma plug might be more appropriate), or (3) dissociate methanol in the chamber near the spark plug.

The ability of any of these (or any other) approaches to provide sufficient dissociation gas necessary to exceed the MRD level is unknown. However, future work on either extending the lean limit or evaluating fractional dissociation should consider the following conclusions.

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*Organic Matter (OM) values were determined by a standard LDV FID. The OM values calculated include the weight of oxygen in the hydrocarbon density of the exhaust. The density value used was 37.69 g/cu ft (vs. 16.33 g/cu ft for gasoline HC). No correction for the FID response to methanol was applied.

B. Conclusions

1. Future work with dissociation should use weight fractions of the components for comparison work. It was found to be particularly useful to separate the hydrogen weight fraction (HWF) for lean limit correlations.

2. Efficiency values can change based on the energy accounting technique used. In general, it is recommended that the actual results be the primary units and simulated results be secondary, however, the specific techniques used should be described.

3. Moderate improvements in brake efficiency are possible with small fractions of methanol dissociation. Improvements up to 10 percent (simulated - 5 percent actual) were observed with a 30 percent fraction.

4. There appears to be a threshold or minimum required dissociation (MRD) level that is necessary before improvements can be obtained with lean mixtures. This hypothesized MRD level may change with speed and load.

5. OM and CO emission levels seem to be influenced by the MRD level. NOx seems only dependent on equivalence ratio.

6. A dissociation reactor has the potential to effectively enhance the energy content of the fuel by about 16 percent above that obtained from lean operation, but only if all of the fuel reaching the engine is dissociated, and consists of predominately hydrogen and carbon-monoxide in their equilibrium proportions. The potential improvement would be correspondingly less if the dissociation process were not complete. For our fraction of dissociation with equilibrium concentrations, the maximum enhancement would be expected to be on the order of 5 percent.

Supporting Analyses

and

Technical Information

III. Test Set-Up

The engine used for this test series was a standard 2 liter Nissan NAPS-Z engine (with electronic port fuel injection -EFI) modified for methanol use. The compression ratio was 12.8:1. Minimum timing for best torque (MBT) was used throughout the test series,* and exhaust gas recirculation was eliminated.

The hydrogen and carbon monoxide (H_2/CO) gas mixture was obtained from compressed gas cylinders and the cylinders were gravimetrically analyzed ($\pm$1 percent) to assure an accurate indication of H_2/CO split. The heating value of the mixture was then calculated on this split based on the heating values of the pure components. (See Table III-1, for more details see Appendix III.)

Table III-1

Net Heating Values**
of Fuels Used

Compound	Net Value (LHV) (BTU/lb)
H_2	51,743
CO	4,328
Mix	10,039
Methanol	8,644

**see Appendix III

The H_2/CO mixture entered the engine through the passage normally used for the hot idle compensator circuit (see Figure 1). This location is slightly upstream of the EFI throttle valve and between the throttle valve and the EFI air meter. An alternate location was briefly attempted, but time pressures prevented a thorough investigation. The alternate location was through the stock EGR entrance to the inlet manifold.

Because of the quantities of H_2/CO gas mixture required to achieve even moderate dissociation rates, only lower power

*MBT was used throughout the series when attainable; in many cases timing was not advanced past incipient detonation, even though more advance would have been required to achieve true MBT.

points were considered for investigation. Since technical personnel from one automobile manufacturer had previously suggested that a test point of 38 psi BMEP at 1500 RPM was representative of overall in-vehicle engine performance, we selected that point as one of our two test conditions. For this engine, 38 psi BMEP and 1500 RPM works out to be approximately 8 BHP or approximately 29.5 ft. lb. of torque (Load 1). The second test condition was arbitrarily selected at 10 ft. lb. (Load 2) and 1500 RPM to give us potentially greater flexibility to achieve higher dissociation rates (because of limited H_2/CO flow rate capability).

Emission measurements were dilute bag measurements. A standard light-duty vehicle (LDV) critical flow venturi (CFV) CVS was used. However, due to the increase in water vapor from the methanol engine, a refrigeration trap was installed in the sample line between the probe and the sample bags. The sample bags were analyzed with a standard LDV analytical system which included a non-heated FID HC analyzer.

IV. Engine Operation

Engine operation with the H_2/CO gas mixture did not differ in any quantitative way from operation with neat methanol. From a qualitative aspect the only observation apparent was that the engine seemed to run smoother with the H_2/CO gas than neat fuel between an equivalence ratio of about 0.7 to about 0.58. Below 0.58 overall equivalence ratio, the engine would not consistently operate smoothly, regardless of dissociation rate utilized (The highest rate attempted was 30 percent at 29.5 ft-lb).

V. Results

A. Efficiency, Load 1

The testing with H_2/CO was performed in two series of tests. The first series was tested at the 29.5 ft-lb condition with fixed H_2/CO flow rates of 15, 30, and 60 SCFH. These flow rates correspond to dissociation rates of approximately 4, 9, and 18 percent by mass of the neat methanol fuel flow in the baseline condition for the range of equivalence ratios tested (i.e., there was sufficient latitude to adjust the liquid methanol flow rates to achieve various equivalence ratios at a fixed H_2/CO flow without disturbing the approximate mass percentages of 4, 9, and 18). After the results of the first series were analyzed, the second series were run repeating the 60 SCFH H_2/CO flow rate and adding a test point at approximately 100 SCFH (30

percent simulated dissociation). These two test points (18 percent and 30 percent dissociation) were run at both the 29.5 ft-lb condition and the 10.0 ft-lb test condition. (Lower H_2/CO flow rates were used to maintain approximately 20 percent and 34 percent simulated dissociation conditions at the lower load point.) Baseline testing was performed before the first series of H_2/CO testing, between the two series, and after the second series. Standard fuel consumption data was taken for all tests, however emissions data were only taken on the first series of tests.

The results were analyzed by segmenting the equivalence ratio into discrete regimes (see Table III-2). Within these small regimes, data was treated as if all the data in that regime had an equivalence ratio equal to the central value of that discrete segment.* With this technique, data with only minor differences in equivalence ratio could be more easily evaluated with standard statistical routines. All of the data reported (including data plots), then, represent the average results within a given segment of equivalence ratios. The only exception to this technique were the emission results. Because of the limited amount of data, all of the data is scatter-plotted on the plots of emission data.

Table III-2

Equivalence Ratio Segments

Range	Segment Value
.455- .500	.478
.501- .545	.523
.546- .590	.568
.591- .625	.618
.626- .665	.647
.666- .735	.701
.736- .765	.750
.766- .805	.780
.806- .855	.830
.856- .904	.878
.905- .955	.940
.956-1.004	.999

*The equivalency ratio segments were selected based on previous results with our specific A/F ratio control system for the EFI system. The segments correspond to the specific positions on the control box which accounts for the slightly non-uniform spacing of the segments and equivalency values. Most data tends to be near the central value of the segment. See Appendix I for the derivation of the stoichiometric fuel-air ratio.

At the 29.5 ft.-lb. test point, even small amounts of simulated dissociation gas show some change in engine BTE performance. Figure 9 shows the results of 4 percent and 9 percent simulated dissociation. The lean limit was extended somewhat with the H_2/CO gas, but no improvement in thermal efficiency was observed at the 4 percent level. Only a slight improvement was observed at 9 percent. Modest improvements were observed at the 18 percent and 30 percent level (see Figure 3).

B. Efficiency, Load 2

The 10 ft-lb load point results seem to have more mixed results than the 29.5 ft-lb data. Table III-3 indicates these results. The efficiency improvements with 20 percent dissociation are what might be expected, but the negative improvement in BTE with the 34 percent dissociation was completely unexpected. If we arbitrarily group the similar dissociation rates at the 10 and 29.5 ft-lb points (i.e. 18 and 20 become 20, and 30 and 34 become 30), we can compare changes in efficiency between the two load points (see Table III-4). It is apparent in Table III-4 that the improvements with 20 percent dissociation at the 10 ft-lb load point are similar to those at the 29.5 ft-lb point. However, if we compare the 20 percent curve shape of the 10 ft-lb results (Figure 10) to the shape of the 29.5 ft-lb data (18 percent results - Figure 3), they bear no resemblance to each other, and have effective slopes that are in opposite directions. In fact, the shape and slope of the 34 percent dissociation curve (10 ft-lb) which had a negative improvement bears more resemblance to the corresponding 29.5 ft-lb data than the two 20 percent curves (for the two load points) which showed similar efficiency improvements. This is somewhat puzzling and a hypothesis is suggested later on describing a concept of minimum required dissociation that may explain the slope changes. No satisfactory explanation has been found for the negative improvement in the 34 percent data.

C. Emissions

Emission tests were only run on the first series of tests (4, 9, and 18 percent dissociation at 29.5 ft-lbs). Results of engine-out emissions (i.e. no catalyst) are shown in Figures 11, 12, and 13 for OM*, CO, and NOx respectively. The OM results in Figure 11 for the baseline appear to indicate a

*Organic Matter (OM) values were determined by a standard LDV FID system. The OM values calculated include the weight of oxygen in the hydrocarbon density of the exhaust. The density value used was 37.69 g/cu ft (vs. 16.33 g/cu ft for gasoline HC). No correction for the FID response to methanol was applied.

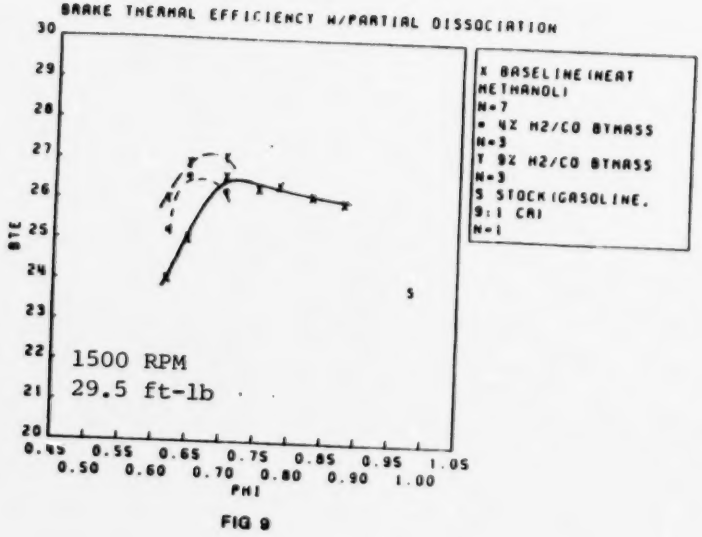

FIG 9

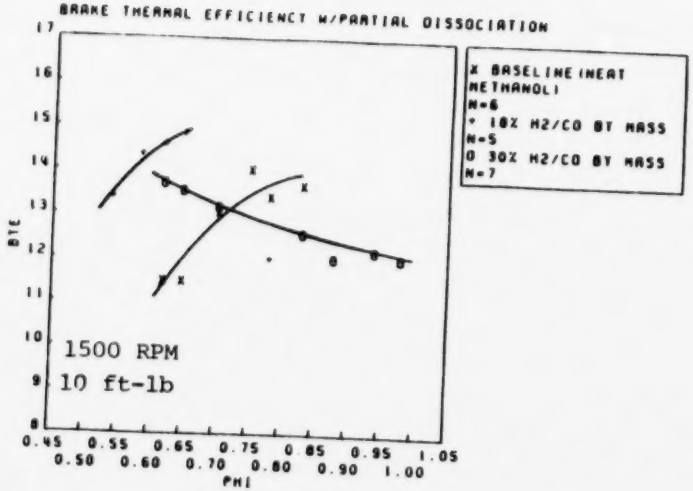

FIGURE 10

Table III-3

Simulated Dissociation at
1500 RPM and 10.0 ft-lb

	Simulated Dissociation Weight Fractions		
	Baseline	20%	34%
% Dissociation			
Energy basis	-	22.48	37.41
Mass basis	-	19.98	33.98
Equivalence Ratio (for best results)	.750	.647	.618
Best Efficiency			
Thermal Efficiency (% BTE)	14.05	14.85	13.72
System Efficiency (% SYE)	14.05	15.35	14.51
Difference	0	.50	.79
% Improvement*			
BTE	-	5.7%	-2.3%
SYE	-	9.3%	3.3%

*Compared to neat methanol baseline

- -

Table III-4

Comparison of Efficiency Changes* at
Two Load Points with Simulated Dissociation

Mass Fraction Dissociated	10 ft-lb	29.5 ft-lb
-BTE		
20%	+5.7%	+ 5.3%
30%	-2.3%	+ 4.6%
-SYE		
20%	+9.3%	+ 8.6%
30%	+3.3%	+10.1%

* Compared to neat methanol baseline.

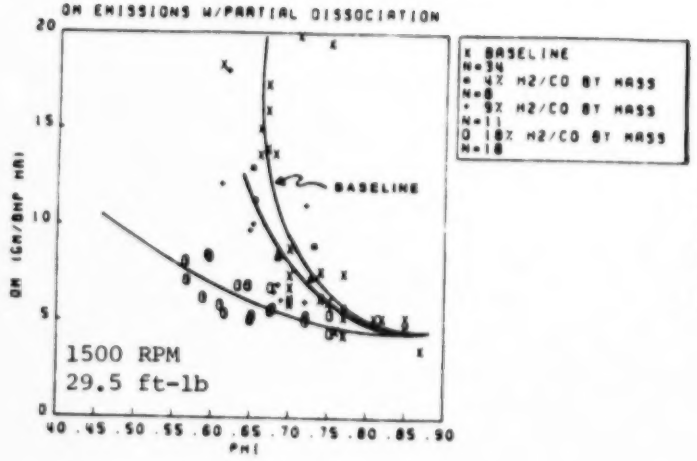

FIG 11

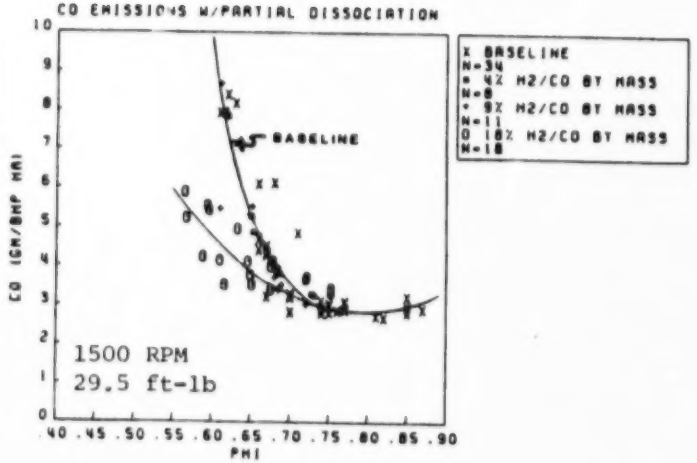

FIG 12

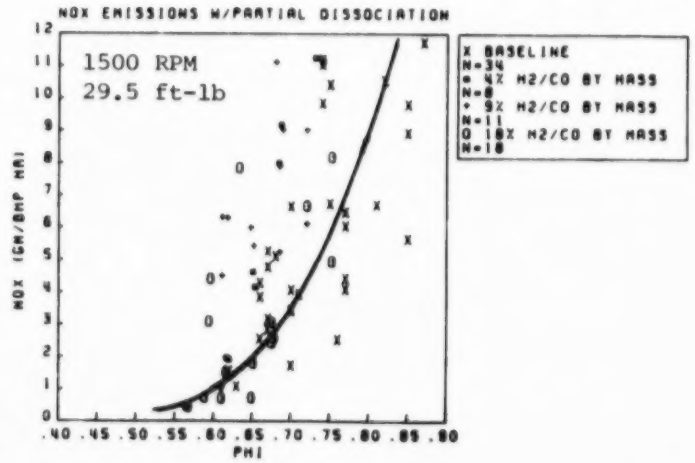

FIG 13

classic case of lean misfire as the equivalence ratio is lowered. Adding small amounts of dissociation gas (4 or 9%) improves the lean misfire limit slightly. Increasing the amount of simulated dissociation to 18 percent, changes substantially the lean misfire limit behavior of the engine. The CO trends (Figure 12) seem to be similar to the OM results. The baseline, 4 percent, and 9 percent dissociation results are for practical purposes the same, while the 18 percent dissociation results are markably different. A hypothesis is advanced later in this report that may explain why the OM and CO results with 18 percent dissociation appear to be different from the results observed for the baseline and lower dissociation percentages.

The NOx results are somewhat less ordered than the OM and CO data. The data in Figure 13 seems to indicate that at the higher equivalence ratios there might be a slight difference in the NOx production levels between using the simulated gas versus using only neat methanol. However, there appears to be no dependence of the NOx level on the amount of H_2/CO gas used. Further, the emissions levels with and without the gas seem to coalesce at the leaner equivalence ratios. NOx levels still appear to depend primarily only on the equivalence ratio used. Since NOx formation can be related to peak combustion temperatures, the data follows the standard combustion theory, and highlights the NOx reduction potential of operating at very lean equivalence ratios.

VI. Discussion

A. Brake vs. System Efficiency

In this report, a distinction is made between Brake Thermal Efficiency (BTE) and System Thermal Efficiency (SYE). Both efficiencies are defined in this report as energy-out per unit time divided by energy-in (E-in) per unit time. The difference is in the manner of determining the value for the amount of energy-in. For BTE, energy-in (per unit time) is defined as the BTU/hr of the simulated dissociation gas consumed plus the BTU/hr of methanol consumed (Equation 1).

$$(1)\quad (E\text{-}in)_{BTE} = (BTU/cu\ ft)(cu\ ft/hr)_{MIX} + (BTU/hr)_{METH}$$

For SYE a different approach was taken. It was assumed that due to conservation of mass, one pound of methanol would produce one pound of H_2/CO dissociation gas. Therefore, the density of the mix could be used to convert the volume flow rate of the H_2/CO simulation gas into a mass rate of gas which would be equivalent to the same mass rate of methanol. This effective mass rate of mix can then be added to the mass rate of methanol used. Multiplying the total mass rate consumed by the energy per unit mass of methanol results in the energy-in (E-in) per unit time (Equation 2).

$$(2)\quad (E\text{-}in)_{SYE} = [(cu\ ft/hr)(lb/cu\ ft)_{MIX} + (lb/hr)_{METH}]\ (BTU/lb)_{METH}$$

The issue between the two methods for computing energy-in is one of control volumes. In our case, we were simulating dissociation with a mixture hydrogen and carbon monoxide (H_2/CO). Therefore the control volume had two energy inputs -- the H_2/CO gas, and the methanol. The total energy-in was the sum of the energy contained in the amount of H_2/CO gas consumed, plus the energy contained in the amount of methanol consumed. The energy of the H_2/CO gas is calculated from the energy in the pure components, and was proportioned by the volume percentage of the component. These values are listed in Table III-1. For this situation Equation 1 would be the appropriate approach to determine energy-in for the purpose of determining what we have chosen to define as brake thermal efficiency (BTE).

In the case of on-board dissociation, the system control volume has only one energy source -- methanol. The creation of the H_2/CO gas from the dissociation catalyst and heat occurs within the control volume. Therefore, in this case it is appropriate to consider Equation 2 as the proper method to determine the amount of energy-in. By using equation two in this manner, we can predict the engine performance as if we had used an on-board dissociation reactor. Note however,

that Equation 2 assumes that the conversion process from one pound of methanol to one pound of dissociation gas is complete. Therefore, Equation 2 represents an upper limit of improvement which would be modified by the completeness of the dissociation. In order to distinguish the actual engine performance from the upper limit of predicted performance, we defined the actual performance as Brake Thermal Efficiency (BTE), and the upper limit as System Thermal Efficiency (SYE).

Creating this distinction between BTE and SYE leaves us in the somewhat awkward position of having two energy values for the same compound (see Table IV-1). The difference between the two energy values is approximately 16 percent (for complete dissociation). What this information suggests is that the energy enhancement of dissociating methanol completely is approximately 16 percent over that of running the engine entirely on H_2/CO gas supplied from some other source.

Table IV-1

Effective Net Heating Values*

Units	BTE w/simulated mixture	SYE w/actual dissociation	Diff. (BTE/SYE)
BTU/lb	10,039	8644	16.1%
BTU/cu.ft.	285	245.4	16.1%

*see Appendix III

The testing for this evaluation used the equivalent of only a portion of the total engine fuel flow for dissociation. An important question in this evaluation was then, "would small amounts of dissociated fuel (assuming high dissociation efficiencies) be beneficial?" If we assumed that improvements in SYE over BTE were linear with the amount of dissociation (assuming that the percent dissociation represents complete dissociation of an equivalent amount of liquid fuel as opposed to the partial dissociation of a larger amount of fuel), we could predict the upper limit of improvement of an onboard reactor over our simulation with H_2/CO gas. A comparison of this linear projection versus the actual results in Table IV-2 suggest that the improvement is not linear. The actual results from this limited data average a 7.3 percent improvement over the linear projection. Therefore, it appears that the change-in-state energy change allows the engine efficiency to improve more

rapidly with lower levels of dissociation. But because the overall improvement due to the change-in-state is limited, the rate of improvement [(SYE-BTE)/BTE] due to energy enhancement will therefore decrease as the fraction of total fuel that is dissociated approaches 100 percent. This analysis, then, tends to support the intuitive conclusions one draws from Figure 5.

Table IV-2

Effects of Energy Enhancement on SYE Compared to BTE With H_2 /CO

	Linear Projection				Actual*	
Load	18%	20%	30%	34%	18%/20%	30%/34%
10 ft lb	-	3.2%	-	5.5%	3.4%	5.8%
29.5 ft lb	2.9%	-	4.8%	-	3.1%	5.3%

* From Table II-1 and Table III-3, (SYE-BTE)/BTE.

Reviewing the theoretical increase in overall engine efficiency due to dissociation, we find there are two apparent sources of efficiency improvements in the overall results. First there are the efficiency improvements strictly from the addition of the H_2/CO gas. This improvement appears to be primarily due to the ability to run the engine leaner as indicated in our BTE results (see Figure 3). Modest BTE improvements at these low H_2/CO flow rates are possible (around 5 percent improvement - see Tables II-1 and III-3). The second source of efficiency improvement is from the increased energy potential of the fuel which would be created by an on-board dissociation reactor (i.e., the difference between BTE and SYE). Table IV-2 and Equation 2 suggest the degree of this second form of improvement is a function of the amount of fuel dissociated and not necessarily the equivalence ratio. Potential improvements due to this second phenomenon at our low simulated rates are of the same magnitude as the first effect (4 percent average improvement - see Table IV-3). However, the relative contribution of the second effect to the overall efficiency would be expected to decrease as the fraction of dissociation increases since this affect appears to be limited to approximately 16 percent overall improvement (Table IV-1). Also, the improvement would be an upper limit of improvement for our dissociation rates since the analysis assumes complete conversion efficiency for each fraction of total engine fuel flow dissociated. The overall efficiency

improvement from dissociating methanol is then the sum of the two effects - hydrogen addition and the energy enhancement - one a function of the fuel-air ratio that can be achieved with the benefit of a given fraction of dissociation, the other a function of the fraction dissociated.

Table IV-3

Sources of Efficiency Improvement

Source		Average Improvement*
BTE	(hydrogen addition)	5.2
SYE	(simulated energy enhancement)	4.1
overall	(simulated dissociation)	9.3

*Average values from Table III-2 (30 percent dissociation data at 10 ft-lb was not included in the average)

B. Lean Limit

In discussing engine operation, it was noted that it was difficult to operate the engine at an equivalence ratio leaner than 0.58 under any of the dissociation fractions tested. We had not expected this result since the engine was baselined at as low as 0.62 equivalence ratio on neat methanol (see Figure 2), albeit at a lower efficiency than with the dissociation gas. Prior to testing the simulated dissociation, we expected that there might be sufficient hydrogen to extend the lean limit more than the extension observed.

A review of explosive limits indicates that the lower limit for methanol is around 6 percent by volume (9). This would translate into an equivalence ratio of 0.46 (see Appendix II) for the limits of combustion. From this information and information from a contract with Ricardo (12) (which demonstrated good efficiency with an HRCC methanol engine at an equivalence ratio down to 0.6), we expected that adding hydrogen (which has a lean limit of 0.1) to the engine would improve the lean operating limit.

The fact that the operational limit was not extended lead us down several paths, some more fruitful than others. One approach was to evaluate the partial equivalence ratio of the hydrogen, and the partial equivalence ratio of methanol. The concept was to evaluate the relationship of each compound to

its flammability limit as the overall mixture was leaned. However, the comparison of our data and that from the relevant literature to the partial equivalence ratio approach was inconclusive. In general, not enough data could be gleaned from the literature to fully evaluate this hypothesis, but the available information suggested that this particular approach may not be worth pursuing further.

The exercise did, however, provide an important perspective on the necessity to do all comparisons based on the weight fraction of the fuel components. There is a reasonable amount of literature on hydrogen supplemented engine operation (3)(4)(5)(6)(7)(8). However, the majority of the work used gasoline (generally Indolene) which was supplemented by hydrogen or some mixture containing hydrogen. In most cases, the data were only available in the form of hydrogen energy fraction (HEF). In order to compare these data to our data it was necessary to convert the HEF to a hydrogen weight fraction (HWF). The following formula* was used to convert HEF to HWF for mixtures of hydrogen and gasoline or hydrogen and methanol.

$$(3) \qquad HWF = R\,(1/[(1/HEF) + R - 1])$$

where

HWF = hydrogen weight fraction
HEF = hydrogen energy fraction
R = the ratio of the energy content of the base fuel to the energy content of hydrogen

Component	Energy content (BTU/lb)**
H_2	51743
Methanol	8644
Indolene	18579

By plotting this equation (Figure 14), we can see an interesting, but probably obvious, phenomenon. If we were to present the our data in terms of hydrogen energy fraction (HEF) as in Parks' (3) and MacDonald's (4) papers (MacDonald also provided HWF), we would have significantly different

---

* Derivation is from HEF = HE/TE
where HE = hydrogen energy = (HWF)(energy content H_2)
TE = total energy = (HWF)(energy content H_2) + (1-HWF)(energy content base fuel)

**see Appendix III

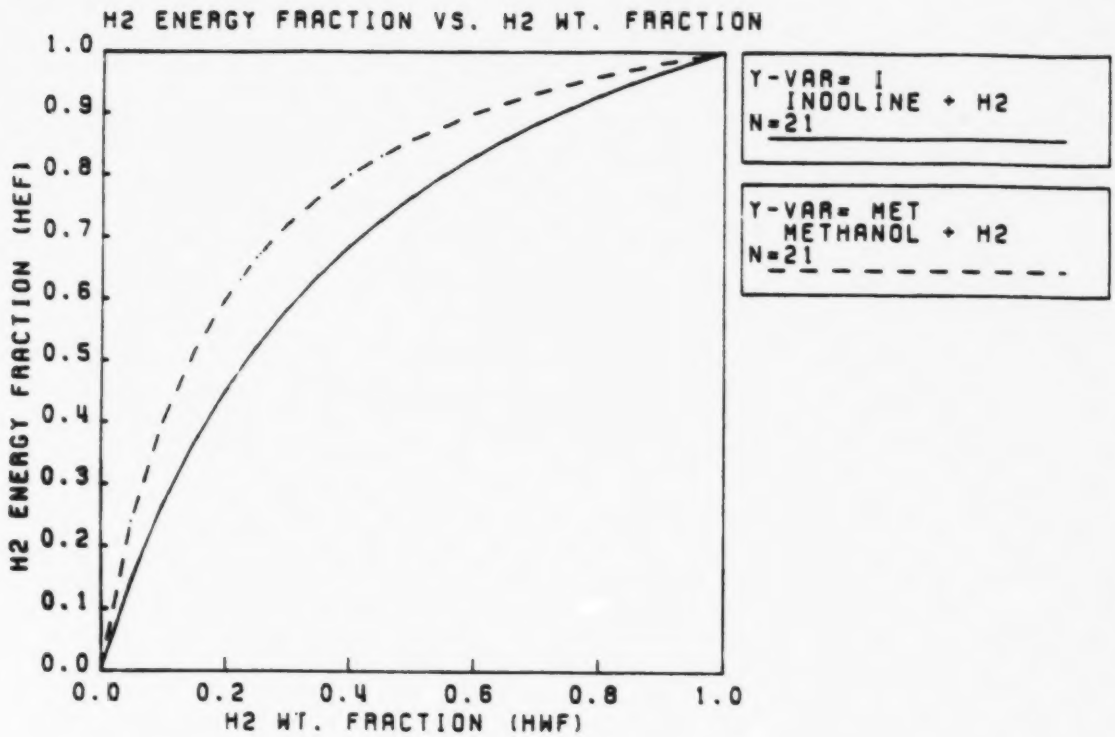
H2 ENERGY FRACTION VS. H2 WT. FRACTION
H2 ENERGY FRACTION (HEF)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0.0
0.2
0.4
0.6
0.8
1.0
H2 WT. FRACTION (HWF)
Y-VAR= I
INDOLINE + H2
N=21
Y-VAR= MET
METHANOL + H2
N=21

FIG 14

weight fractions for the same energy fraction because the major component in our fuel differs from the fuel used by Parks and MacDonald (methanol versus Indolene). Therefore, because the stoichiometric fuel-air ratio must be determined on a weight basis, it was necessary to make comparisons with the literature references based on the hydrogen weight fraction (HWF), and not the hydrogen energy fraction (HEF), in order to compare the results when different fuels or mix of fuels was used.

This insight lead to the possibility that we might be able to correlate the engine lean limit with the HWF, and ignore the effect of the CO on the lean limit. Table IV-4 tabulates these data from references (1), (3), (4), and (5). (Note HEF values from these references were transformed into HWF values by the equation 3.) Plotting the data from Table IV-4 for the mixture of hydrogen and methanol or gasoline (Figure 15), we appear to have a reasonable correlation* between lean limit and the hydrogen weight fraction (HWF) of the fuel. We further note that extrapolation of these correlation lines for either methanol or gasoline in Figure 15 (R^2 = .9 to .97) to an HWF of 1.0 (100 percent H_2) would not yield the lean limit value of 0.18 (3) for pure hydrogen. This suggests that the improvement in lean limit is not linear over the entire range of hydrogen supplementation and the non-linearity is indicated in Figure 16. Even so, because of the good correlation of the data in Figure 15, we can infer that the linear regression is a reasonable approximation of the behavior over the limited range of HWF's investigated. We should also note that the equilibrium HWF which would result from complete dissociation is limited to a value of approximately 0.126 because of the presence of the carbon monoxide.

From Figure 15, it is relatively easy to surmise why we were having difficulty operating the engine leaner than 0.58 equivalence ratio. Even with 30 percent mass fraction of H_2/CO simulated dissociation gas, we had only 3.6 percent mass fraction of H_2 (HWF). At this level of HWF, Figure 15 seems to suggest that if we wish to significantly extend the lean limit, then the HWF must be increased. If the HWF were increased up to the maximum allowed by complete dissociation, the equivalence ratio at the lean operational limit of the engine might be expected to approach the flammability limit of the dissociation mixture, but the degree would depend on the engine design.

---

*Note: Because data from Houseman's paper did not appear to agree with the other gasoline data (possibly because of the effects of other constituents) it was not included in the linear regression of gasoline-hydrogen mixtures. A separate regression of Houseman's data by itself correlates well with HWF.

Table IV-4

Lean Limit Equivalence Ratio
vs.
Hydrogen Weight Fraction

Investigator/Fuel	HWF	Lean Limit
Clemmens (Methanol)	0	.618
	.005	.618
	.011	.618
	.022	.583
	.036	.583
Hirota (Methanol)(1)	.112	.435
Parks (Gasoline)(3)	0	.7
	.051	.6
	.097	.5
	.25	.34
MacDonald (Gasoline)(4)	.144	.42
Houseman (Gasoline)(5)	0	.71
	.023	.61
	.046	.59
	.068	.52
Parks* (H_2)	1.0	.18

* Parks (3) indicates (in his Table B-1) that the lean limit with pure hydrogen is 0.18 in a CFR engine.

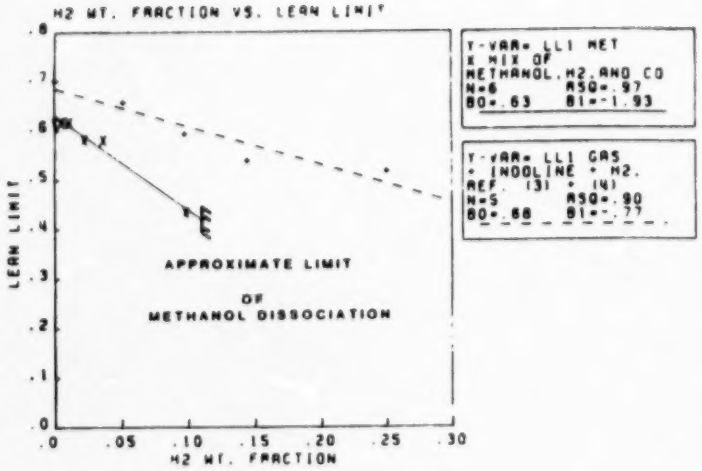
H2 WT. FRACTION VS. LEAN LIMIT
LEAN LIMIT
H2 WT. FRACTION
APPROXIMATE LIMIT
OF
METHANOL DISSOCIATION
Y-VAR= LL1 MET
X MIX OF
METHANOL, H2, AND CO
N=6
RSQ=.97
B0=.63
B1=-1.93
Y-VAR= LL1 GAS
+ INDOLINE + H2.
REF. (3) + (4)
N=5
RSQ=.90
B0=.68
B1=-.77

FIG 15

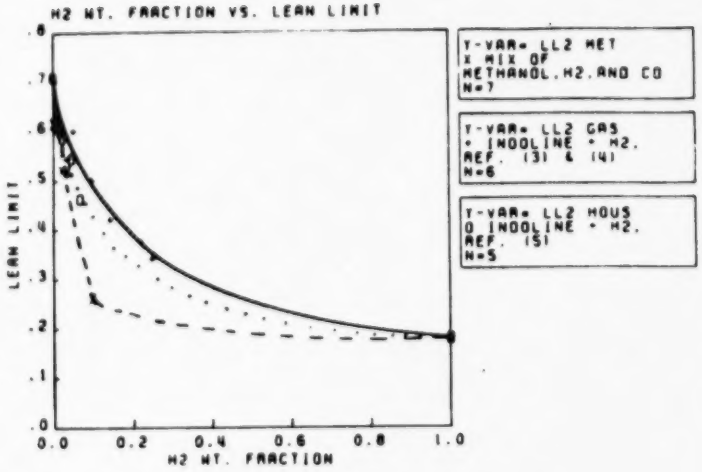
H2 WT. FRACTION VS. LEAN LIMIT
LEAN LIMIT
H2 WT. FRACTION
Y-VAR= LL2 MET
X MIX OF
METHANOL, H2, AND CO
N=7
Y-VAR= LL2 GAS
+ INDOLINE + H2.
REF. (3) & (4)
N=6
Y-VAR= LL2 HOUS
O INDOLINE + H2.
REF. (5)
N=5

FIG 16

C. Minimum Required Dissociation (MRD)

In determining the fraction of dissociation required to obtain meaningful results, previously we had seen in Figure 3 and Figure 9 that 18 percent and 30 percent simulated dissociation provided somewhat greater improvements in BTE over smaller fractions of dissociation (i.e., stock, 4 percent, and 9 percent). It is probably intuitively obvious that the more H_2/CO utilized in the engine (ie. higher HWF), the better the BTE would be. The data does tend to support this conclusion, but when separating the data by equivalence ratio groups versus the fraction of dissociated methanol, an interesting picture emerges. The limited data plotted in Figure 17 suggest that a minimum required dissociation (MRD) rate of around 12.5 percent to 13 percent apparently is necessary to show an improvement in BTE with leaner mixtures. The same results appear in Figure 18 for SYE which is on the same basis as Hirota's (1) data. Below about 13 percent, and at extremely lean mixtures (less than 0.65), the projected BTE results (Figure 17) are substantially lower than optimum neat methanol results (26.6 percent BTE, see Table II-1). Above the apparent 13 percent minimum dissociation value, the leaner mixtures are projected to outperform neat methanol with the exception of the 0.7 equivalence ratio. It is interesting to note that for this ratio (see Figure 17) the slope of the regression line of BTE versus percent dissociated is nearly a horizontal line (0.01 BTE points per fraction of H_2/CO). The slope of regression line suggests that regardless of how much of the fuel delivered to the engine is dissociated methanol, the thermal efficiency remains relatively constant (at an equivalence ratio of 0.7). When considering this situation from a system efficiency basis (Figure 18), the outlook is somewhat more promising with a projected 0.05 SYE point increase for each 1 percent increase in dissociated gas. If the linear relationships shown in Figures 17 and 18 were valid for the entire range up to dissociation of 100 percent of the total energy supplied, we would expect a 3.6 percent improvement in BTE (18.8 percent SYE) at 0.7 equivalence ratio. An 18.8 percent improvement in SYE over our base of 26.5 percent BTE with neat methanol would result in an SYE of 31.61 percent. This value is in close agreement* with Hirota's (1) results

* Values interpolated from Hirota's paper are 30 percent SYE for 0.769 equivalence ratio, and 32 percent SYE for 0.667 equivalence ratio. Our calculated value is 31.61 percent SYE for 0.7 equivalence ratio.

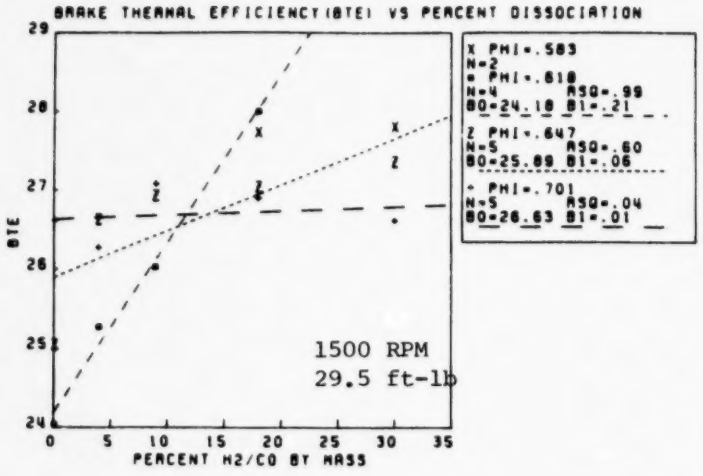

FIG 17

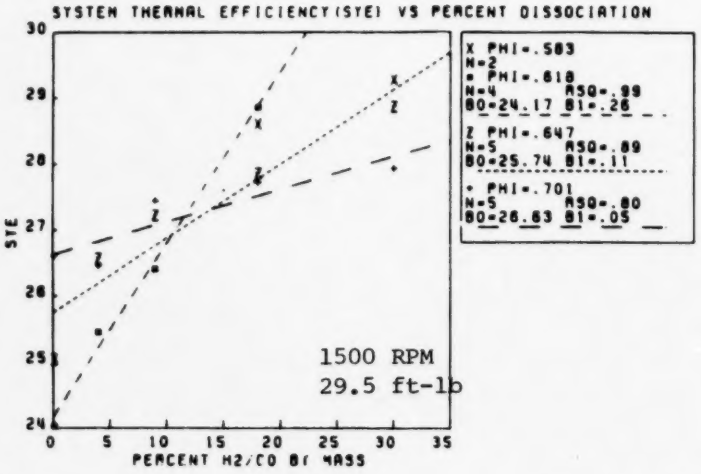

FIG 18

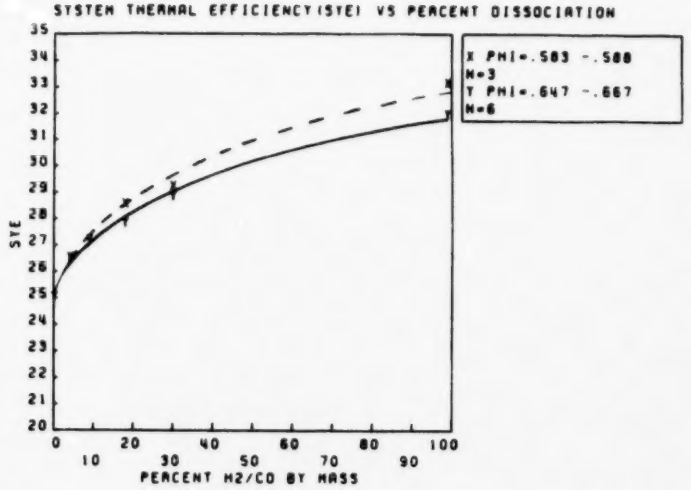

FIG 19

for 100 percent dissociation*. However, if the above analogy is applied to the leaner equivalence ratios, the results predicted by the slope of SYE improvement are implausible. Therefore, one must assume that the change in SYE with increasing fractions of dissociation is not linear.

By plotting Hirota's values with our data (see Figure 19), it seems that for lean equivalence ratios (less than 0.7) the data appears to follow an exponential curve. Therefore if the improvement in SYE decreases exponentially with increasing fractions of dissociation, the case of a relatively small overall improvement in SYE (i.e., a relatively flat curve) might be approximated by a straight line as appears to occur for an equivalence ratio of 0.7. For leaner mixtures, the curve appears to have more "bow" to it, and the straight line analogy (based on a linear regression of the data on the front part of the curve) falls apart.

The exponential shape might support and explain the data in Figures 17 and 18 (minimum dissociation to show improvement) in the following manner. If combustion at below the apparent inflection point of 12 to 13 percent dissociated fuel were dominated by methanol combustion reactions then one would expect the BTE for these lower dissociation levels and at equivalence ratios leaner than 0.7 to reasonably duplicate the baseline case (i.e. no dissociation). A review of Figure 20 suggests that although the rate of fall-off in BTE at these lean equivalence ratios with low fractions of dissociation is not as rapid as with neat methanol, the fall-off does somewhat parallel the neat methanol results. Above this inflection point, it is hypothesized that there is sufficient hydrogen, along with a lack of methanol at these lean ratios, to support a hydrogen initiated flame front within the combustion chamber. The assumed hydrogen flame front would then set off the lean methanol mixture. In other words, one could phrase this hypothesis as "moderate fractions of dissociation serve as an ignition enhancement system for extremely lean methanol operation."

The data at this one load point is, of course, not sufficient to predict if such an inflection point would occur at other speed and load points at the same value of MRD or even occur at all. Recognizing that even if 100 percent of the energy

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*Note: Hirota (1) used a similar engine to the one used in our study. He used a Nissan L20 engine and we used a Nissan Z20 engine, the short block assemblies are essentially the same with the major difference in engines being in the cylinder head.

passed through a dissociated reactor, 100 percent of the methanol would probably not dissociate under the most optimum conditions (and even less at part throttle). It may be critically important that: 1) there could be a minimum amount of hydrogen necessary to achieve a hydrogen initiated flame front when dissociated methanol is used for fuel, and 2) there could be a switch between the hydrogen initiated flame front and a methanol initiated flame front at different dissociation levels with different optimum fuel-air ratio requirements for each regime.

The previously described "minimum required dissociation" (MRD) hypothesis might also provide a possible explanation for the mixed results at the 10 ft-lb load point. If we compare the 20 percent data in Figure 22 for 10 ft-lb, not to the 18 percent data in Figure 21 for 29.5 ft-lb, but instead to the 9 percent data in Figure 20 (for 29.5ft-lb), we see similar curve shapes. Recognizing that the apparent inflection point between having sufficient dissociation gas for lean operation and not having sufficient quantity of gas was around 13 percent for 29.5 ft-lb, the 9 percent and 18 percent flow rates for the 29.5 ft-lb load point fall on either side of this apparent inflection point (Figure 20 and 21). Is it coincidence that they also have opposite slopes of their efficiency versus equivalence ratio curves in the same f/a ratio regime? If there is a cause and effect relationship occurring, then it might be possible that the opposite slope of the 20 percent and 34 percent curves at 10 ft-lb load point (Figure 22) may indicate that the inflection point for MRD may have moved from 13 percent at 29.5 ft-lb to between 20 percent and 34 percent for the 10 ft-lb load point.

VII. Postscript

In summing up, we can say that this program demonstrated that the basic question, "Is it possible to achieve a significant portion of the theoretical potential of full dissociation with a less complex system?" appears to be able to be answered in the affirmative assuming that the fractional dissociation equipment is less complex than the full dissociation system. Overall, up to 40 percent of the potential efficiency improvement was achieved with only a 30 percent fraction of dissociation. However, the actual improvement was, under the best conditions, only a modest 10 percent improvement. Future work in this area should be cognizant of the simulation effects (BTE vs. SYE), the apparent dependency of the lean limit on HWF, and the potential impacts of the MRD level.

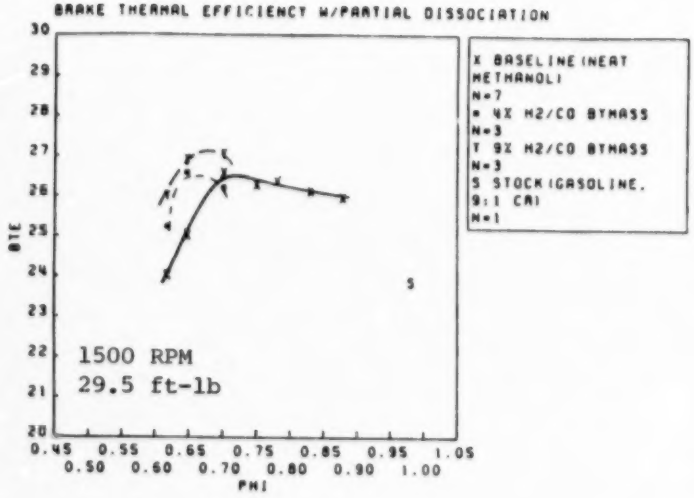

FIGURE 20

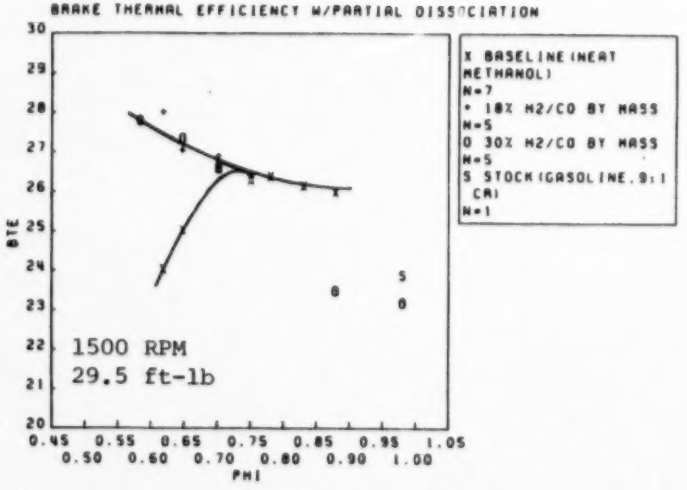

FIGURE 21

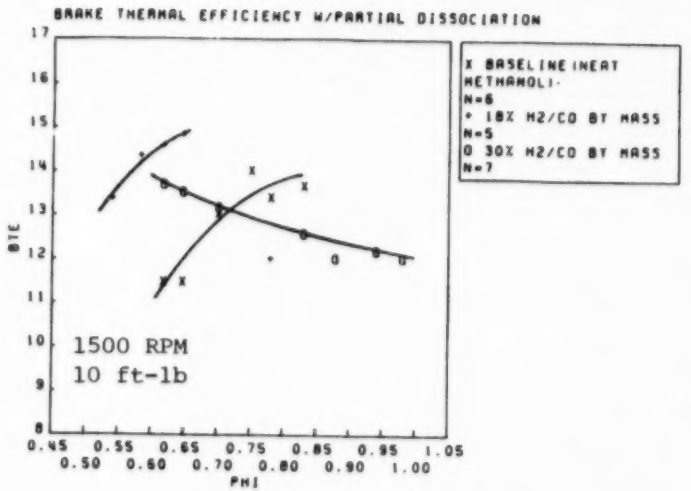

FIGURE 22

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(13) Tokuichi Inagaki, Toshio Hirota, and Zene Ueno, Combustion and Emission of Gaseous Fuel from Reformed Methanol in Automotive Engines, presented at the Alcohol Fuels Technology Third Internation Symposium, Asilomar, California, May 28-31, 1979.

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Appendix I

Stoichiometric Fuel-Air Ratio

A. Simulated Dissociation with Methanol

The stoichiometric fuel-air ratio of the different mixtures can be determined by variations in the chemical equation for complete combustion. The standard form for methanol is

(AI-1) $CH_3OH + (1.5)\ O_2 \rightarrow CO_2 + (2)H_2O$

Note: for simplification, we will consider O_2 as air with a mixture of $(1)O_2 + (3.73)N_2 + (0.4)Ar$, and a molecular weight of 138.09.

The basic dissociation reaction is

(AI-2) $$CH_3OH \xrightarrow[\text{Catalyst}]{\text{Heat}} CO + 2H_2$$

From equation AI-2, we note that the mole ratio of hydrogen to CO 2:1. Therefore, if we were to add dissociated hydrogen and CO to the basic equation (AI-1), the hydrogen and CO would need to reflect this 2:1 split.

(AI-3) $(1-x)CH_3OH + (x)(2)H_2 + (x)CO + (y)O_2 -- (a)CO_2 + (b)H_2O$

where:

x = the mole fraction of the dissociated gas added.

Balancing AI-3, we find that the value for "y" remains the same at 1.5 as in equation AI-1. Therefore, we can say for an equilibrium balance of dissociated hydrogen and CO, the stoichiometric fuel air ratio is the same as liquid methanol. However, in our case, our compressed gas cylinders did not have the exact equilibrium split of H_2 and CO. Instead of the 2:1 H_2 to CO split, we had a 65.65%:34.35% split of H_2 to CO which works out to be a 1.9112:1 split. Substituting this actual split in to AI-3, we have

(AI-4) $(1-x)CH_3OH+(x)(1.9112)H_2+(x)CO+(y)O_2--(a)CO_2+(b)H_2O$

Balancing this equation, we find that "y" is a function of "x" - the mole fraction of the dissociation gas.

(AI-5) $$y = 1.5 - (0.0444)(x)$$

Converting each reactant on the left side of AI-4, substituting AI-5, and forming a ratio of the fuel reactants to the air reactants in AI-4 provides us with the stoichiometric fuel-air ratio for our split H_2 and CO with methanol

(AI-9) $$(f/a)_s = \frac{[(1-x)(32.043)+(1.9112)(x)(2.016)+(x)(28.011)]}{[1.5 - (0.0444)(x)]\ (138.09)}$$

Where the molecular weights are:

CH_3OH = 32.043
H_2 = 2.016
CO = 28.011
Air = 138.09

By substituting various values for the percent dissociation (values for "x") in equation AI-9, the effect of the percent dissociation on the stoichiometric f/a ratio can be determined. For instance, for "x" values of 9% dissociation (0.09) and 30% dissociation (.30) the computed stoichiometric values are 0.1550 and 0.1558 respectively. Since these values compare to within 1% of the stoichiometric ratio of 0.1547 for liquid methanol, the slight offset in the stoichometric ratio for the dissociated gas was ignored in this report, and all equivalence ratios were based on the liquid methanol value rounded off to 0.155.

The hydrogen weight fraction (HWF) for our mix of hydrogen and CO from compressed cylinders plus liquid methanol is determined by:

(AI-10) $$HWF = \frac{(1.9112)(x)(H_2)}{[(1-x)(CH_3OH)+(1.9112)(x)(H_2)+(x)(CO)]}$$

where: the molecular weights from AI-9 would be substituted for H_2, CO, and CH_3OH

For the case where the engine were supplied with 100% gas from an equilibrium dissociation of liquid methanol, the HWF would be found by:

(AI-11) $HWF = (2)(H_2)/[(2)(H_2) + (CO)]$

The HWFs in table form for the percent dissociations used in this study with compressed H_2/CO simulation gas are in Table AI-1.

Table AI-1

Hydrogen Weight Fraction

% Dissociation	HWF
.04	.005
.09	.011
.18	.022
.30	.036
.34	.041
1.0*	.121
1.0**	.126

* Simulation gas in compressed gas cylinders
** Equilibrium dissociation of liquid methanol

B. Dissociated Methanol

Because dissociated methanol contains several components other than H_2 and CO, equation AI-9 is not appropriate to calculate the fuel-air ratio of the products from a dissociation reactor. However, Hirota's paper (1) provides a chemical analysis of typical products from a dissociation reactor. Using Hirota's volume analysis and a modified form of equations AI-3 and AI-4, we can derive the weight fraction of each component which is necessary to balance a chemical equation with these constituents. Table AI-2 lists Hirota's analysis.

Table AI-2

Composition of Dissociation Gas (1)

Compound(i)	MW	V(i)*	H(i)	C(i)	O(i)
H_2	2.016	.63	2	0	0
CO	28.011	.24	0	1	1
CH_3OH	32.043	.05	4	1	1
CO_2	44.011	.04	0	1	2
CH_3OCH_3	46.070	.03	6	1	1
CH_4	16.043	.01	4	1	0

*Volume fraction determined by analysis of dissociation gas (1).

Rather than write out a long formula with these compounds, we can write a simplified equation that just counts the hydrogen, carbon, and oxygen in the fuel irrespective of the chemical compound.

(AI-12) $(e)C + (f)H + (g)O + (y)O_2 = (a)CO_2 + (b)H_2O$

where:

e = 0.4 = the sum of the products of C(i) times V(i)
f = 1.68 = the sum of the products of H(i) times V(i)
g = 0.4 = the sum of the products of O(i) times V(i)

Balancing equation AI-12, we have

a = 0.4
b = 0.84
y = 0.62

The stoichiometric fuel-air ratio is simply the ratio of the weight of the fuel reactants in AI-12 to the weight of the air reactants (note: O_2 can be considered to be air with a MW of 138.09). The weight of the fuel reactants is simply the number of atoms for each fuel reactant times the molecular weight (MW) for that reactant (note: (g)O (fuel oxygen) is considered fuel). Mathematically this would be expressed as

(AI-13) $$(f/a)_s = \frac{[0.4(12.011) + 1.68(1.008) + 0.4(16)]}{(0.62)(138.09)}$$

(AI-14) $(f/a)_s = .1506$

We note that stoichiometric value for Hirota's mixtures requires approximately 2.6% less fuel than the liquid methanol fuel-air ratio of 0.1547. We also note that the hydrogen-carbon ratio of Hirota's data of 1.68H:0.4C or 4.2:1 HC ratio is about 5 percent greater than methanols 4:1 HC ratio. Therefore, we assume Hirota's analysis has some round-off and approximation errors associated with it. A high hydrogen content would also drive the stoichiometric ratio lean from the liquid methanol value. Because the offset of Hirota's stoichiometric ratio from that of methanol is relatively small, and there is the possibility that Hirota corrected for the offset in reporting his results, we chose to ignore the offset in the presentation of the data.

The hydrogen weight fraction (HWF) for Hirota's fuel mix is determined by:

(AI-15) $HWF = [H(i)][V(i)][H]/[(e)(C) + (f)(H) + (g)(O)]$

Where:

-H(i) and V(i) are form Table AI-2 for H_2
-The molecular weights for H, C, and O are

H = 1.008
O = 16.0
C = 12.011

- -e, f, and g are from AI-12

(AI-16) $HWF = .112$

C. Gasoline

Stoichiometric fuel-air ratios for gasoline-hydrogen mixtures were calculated from the equation listed in Appendix A of Parks' paper (3) - his equation A-1. A ratio of the fuel reactants to the air reactants was formed as indicated

$$(AI\text{-}17) \quad (f/a) = \frac{C_{10}H_{18} + [24HEF/(1-HEF)](H_2)}{([14.5 + (12HEF/(1-HEF)]/PHI)(O_2 + 3.76N_2)}$$

For stoichiometry "PHI" is set equal to 1 and AI-17 becomes

$$(AI\text{-}18) \quad (f/a_s) = \frac{138.25 + [24HEF/(1-HEF)](1.008)}{14.5 + [12HEF/(1-HEF)](138.09)}$$

where: HEF = hydrogen energy fraction*

*When HEF was not given it was calculated from HWF

$$HEF = HWF(EH_2)/[HWF(EH_2) + (1-HWF)(EG)]$$

where:

EH_2 = LHV of Hydrogen = 51743 (BTU/lb)

EG = LHV of Indolene = 18579 (BTU/lb)

The stoichiometric fuel-air ratio calculated for the various gasoline hydrogen mixtures listed in references (3), (4), (5), (6), and (8) are listed in Table AI-3.

Table AI-3

Stoichiometric Fuel-Air Ratio
of Hydrogen-Gasoline Mixtures

Investigator	HEF	HWF	$(f/a)_s$
Parks (3)	0	0	.069
	.13	.051	.063
	.23	.097	.0582
	.48	.249	.0454
MacDonald (4)	.32	.144	.0538
Houseman (5)	.06	.022	.0664
	.11	.044	.0638
	.16	.064	.0616
Jordan (6)	.41	.20	.0491
	.74	.50	.0311
	1.00	1.00	.0292
Hoehn (8)	.29	.13	.0551

Appendix II

Equivalence Ratio at the Lower Flammability Limit

The equivalence ratio at the flammability limit was calculated for several compounds. Included were methanol, H_2, CO, and Indolene.

Typically flammability/explosive limits are presented on a volume fraction basis as opposed to a weight fraction basis. Since the equivalence ratio is based on a mass comparison, the volume based flammability limits must be converted to a mass based fuel-air ratio in order to obtain a mass based equivalence ratio. The Merck Index (9) lists the following volume based flammabilty or explosive limits.

Table AII-1

Volume Based
Lower Flammability/Explosive Limits (9)

Compound	Lower Limit (%)
Methanol	6%
H_2	4%
CO	12%
Indolene (Gasoline)	1.3%

An assumption is made that these limits do not change with pressure, or if they do change the effect is relatively minor. Using this assumption we can then convert the fuel volume fraction to a mass fraction at STP conditions (T = 518.7°R and P = 2116 lb/sqft). First the weight density (w) is computed with equation AII-1. The molecular weight (MW) of the fuel is found in Table AII-2.

(AII-1) $$w = p/RT$$

where

(AII-2) $$R = 1544/MW$$

Table AII-2

Molecular Weights

Compound	MW
Methanol	32.043
H_2	2.016
CO	28.011
Indolene	106*
air	28.966**

Next we form an equation that describes the components in 1 cubic foot of a fuel(f) plus air(a) mixture at the volumetric based lower flammability limit (LFL).

(AII-3) $[(LFL)(cuft)(w)(lb/cuft)]_f + [(1-LFL)(cuft)(w)(lb/cuft)]_a$

= lb mix/cuft mix

Since the fuel-air ratio is simply a ratio the respective weights in AII-3, we can determine the fuel-air ratio at the lower flammability limit by

(AII-4) $(f/a) = [(LFL)\ (w)]_f\ /\ [(1-LFL)\ (w)]_a$

Dividing equation AII-4 by the stoichiometric fuel-air ratio of the fuel in question provides us with the equivalence ratio (phi) at the lean limit. The results are listed in Table AII-3.

(AII-5 $phi_{LML} = (f/a)_{LFL}\ /\ (f/a)_s$

Table AII-3

Equivalence Ratio at the
Lower Flammability Limit

Compound	STOICH (f/a)	LFL (vol %) (9)	phi@ LFL
methanol	.155	6%	.455
H_2	.0292	4%	.100
CO	.4057	12%	.325
Indolene (Gasoline)	.069	1.3%	.700

*Reference (11), note the average molecule is $C_{7.64}\ H_{14.13}$

**Reference (10)

Appendix III

Energy Values and Derivations

Lower heating values (LHV) or net heating values used in this report for pure compounds were obtained from the Merck Index (9) and Obert (14). Values are listed in table AIII-1. The methanol used was industrial grade methanol analyzed at better than 99.9 percent methanol. The analysis for LHV of the methanol actually indicated a value approximately 1.4 percent less than Obert. However, since this test program involved comparative testing with the same fuel, the absolute value of the LHV for methanol was not as important. Furthermore, the magnitude of the difference was relatively small and considered inconsequential relative to engine variability. Therefore, we elected to go with Obert's value which results in more conservative values for engine efficiency.

The LHV for the simulated dissociation mix (H_2/CO) was determined by rationing and summing the ratios of the heating values based on their weight fraction of the total mix. The mass densities were computed from the perfect gas law as indicated in equation AII-1. The weight fractions were then computed as in equations AI-3 and -4. The weight fractions listed with these equations are the values used to compute the LHV ratios. The resultant LHV values of the mix are listed in Table AIII-2.

Table AIII-1

Net Heating Values
of Pure Compounds

Compound	Net Value*(LHV)
H_2 (9)	51,743
CO (9)	4,328
Methanol (14)	8,644
Methanol (ASTM D-240)	8,528
Indolene (ASTM D-240)	18,579

*BTU/lb_m

Table AIII-2

Net Heating Value
of the Simulation Gas

	H_2	CO	Mixture*
Heating Value (LHV)			
(BTU/lb)	51,743.	4328	10,039
(BTU/cu. ft.)	269	315	285
Density (lb/cu. ft.)	.0052	.0727	.02839

*Gravimetric analysis of the gas cylinders used to provide the simulation gas indicated the cylinders contained 65.65 volume percent H_2 and 34.35 volume percent CO. (Analysis accuracy was $\pm$1 percent of point.) Heating value of the mixture in BTU/cubic foot was determined by proportioning the heating value of the pure components based on their volume percentage of the mix. The same was true of the density calculations.